UCRL-TR-207819

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Recent Applications of SPME in Directed Stockpile Work (FY04)

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November 9, 2004

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This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

Recent Applications of SPME in Directed Stockpile Work (FY04)

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Abstract

Solid Phase Microextraction (SPME) has been used to sample non-nuclear materials for analysis by gas chromatography-mass spectrometry (GC/MS). This report summarizes progress in the areas of individual materials' outgassing signatures, microcompatibility tests and analysis of polar analytes.

Introduction

Solid Phase Microextraction (SPME) has been used to sample non-nuclear materials for analysis by gas chromatography-mass spectrometry (GC/MS). Outgassing of compounds that may be incompatible with other weapon materials is a potentially significant factor in system aging and reliability, and SPME is ideal for the collection of trace levels of volatile and semi-volatile organic outgassing species. Laboratory experiments were carried out with the goal of utilizing SPME to non-intrusively collect and interpret trace outgas signatures from organic and high explosive (HE) components within the weapon headspace to help establish lifetimes, identify material aging mechanisms and potential incompatibilities, and to detect contamination. These experiments include small and large scale compatibility tests, collection of individual material signatures, and evaluation of SPME for polar analytes. Relevant data is fed into a mass spectral deconvolution library that is being developed concurrently. This report will summarize progress in FY04 in the areas outlined below.

Individual Material Signatures: In order to construct a database of outgassing signatures of individual organic and polymeric weapon components, samples were collected and prepared for SPME GC/MS analysis. An awareness of material specific outgassing species is needed in order to identify baseline outgassing characteristics. This information should also be a factor in the selection of new or reformulated materials for system rebuilds. In most cases, outgassing species of intact and/or non-defective materials are inert or present in negligible amounts, but the sensitivity of SPME allows the early detection of undesired volatile compounds.

Microcompatibility tests: Compatibility tests with small amounts of materials (a.k.a. microcompatibility tests) are normally conducted with two materials per sample vial followed by aging under different conditions. These types of compatibility tests are designed to flag potentially incompatible materials by identifying degradation products not found in the outgas signatures of the individual materials. Previous work in this area focused on the interaction of polysulfone with select materials and composites (UCRL-TR-206891). Additional tests were carried out to evaluate the interactions of other system materials that had not been studied in FY03.

SPME of polar analytes: Finally, SPME is being evaluated for the identification of polar analytes such as alcohols and carboxylic acids that may be present in some weapon materials. Such compounds could be present as synthesis or processing byproducts, or as degradation products, and this class of compounds has not been targeted in earlier SPME work. The typical SPME-GC setup for LLNL experiments has involved a SPME fiber and GC column combination that is optimized for the majority of anticipated headspace species, which are non-polar to slightly polar compounds (e.g. siloxanes, hydrocarbons); however, polar compounds such as alcohols and carboxylic acids are not readily observed in this analytical setup. The search for polar outgassing products offers an opportunity to collect additional data on the state of weapon materials and thereby form a more complete picture of total outgassing behavior.

Experimental

General sample preparation for SPME-GC/MS analysis: Materials are prepared for SPME headspace sampling by placing either the individual material or two materials (usually 10-100 mg) in a headspace vial that is sealed under nitrogen. Samples are aged at room temperature or 70°C for two weeks prior to analysis.

Automated analysis conditions: Samples are analyzed by SPME GC/MS using an automated system under the following conditions: 75 µm Carboxen-PDMS SPME fiber, conditioned for 20 min at 260°C; headspace sampled at 50°C for 5 min and injected into the GC for 1 min at 250°C. The Agilent 6890 GC is set for splitless injection, purge @ 0.5 min, using a Restek RTX5-MS column (30 m, 0.25 mm ID, 0.25 µm film) with a 1.0 mL/min constant flow of helium. The 20 min run has the following temperature profile: 40°C/2 min, 15°C/min to 300°C, hold 0.67 min. An Agilent 5973 mass spectrometer scans the mass range from 20-450 at a rate of 1.75 scans/sec with a filament delay of 2.75 min.

Polar SPME conditions: Headspace samples are collected manually under the following conditions: 85 µm Polyacrylate SPME fiber, conditioned for 30 min at 300°C; headspace sampled at 50°C for 20 min and injected into the GC for 1 min at 250°C. The Hewlett-Packard 6890 GC is set for splitless injection, purge @ 0.75 min, using a Supelco Nukol column (15 m, 0.25 mm ID, 0.25 µm film) with a 2.0 mL/min constant flow of helium. The 17 min run has the following temperature profile: 40°C/2 min, 15°C/min to 220°C, hold 3.00 min. A Hewlett-Packard 5973 mass spectrometer scans the mass range from 35-500 at a rate of 1.63 scans/sec with a filament delay of 2.00 min.

Results and Discussion

Individual Materials Signatures: The collection of headspace signatures of individual weapon materials was carried out on an ongoing basis in FY04. The materials are listed in Table 1 in the appendix. A gas chromatogram of syntactic polysulfide is shown in Figure 1. The major outgassing

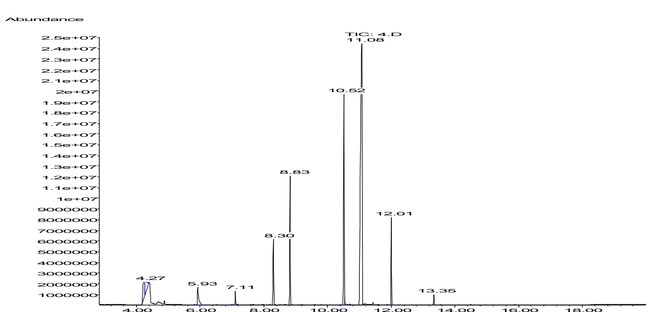

Figure 1. Gas chromatogram of SPME headspace sample of syntactic polysulfide

product is 1,3,6,7-dioxadithionane (RT 11.08 min), a known decomposition product of the polysulfide (Ellerstein, S.M.; Bertozzi, E.R. Encyclopedia of Chemical Technology, 3rd Ed., Vol. 18, 1982, pp 814-831). This is an example of the type of information that can prove valuable in attributing headspace species to specific materials.

<u>Microcompatibility Tests</u>: Microcompatibility tests were carried out on the materials shown in Table 2 in the appendix. For this set of samples, no significant incompatibilities were observed. Figure 2 shows the gas chromatograms of urethane 7200, S5370, and urethane/S5370. As shown in the figure, the two largest peaks in the

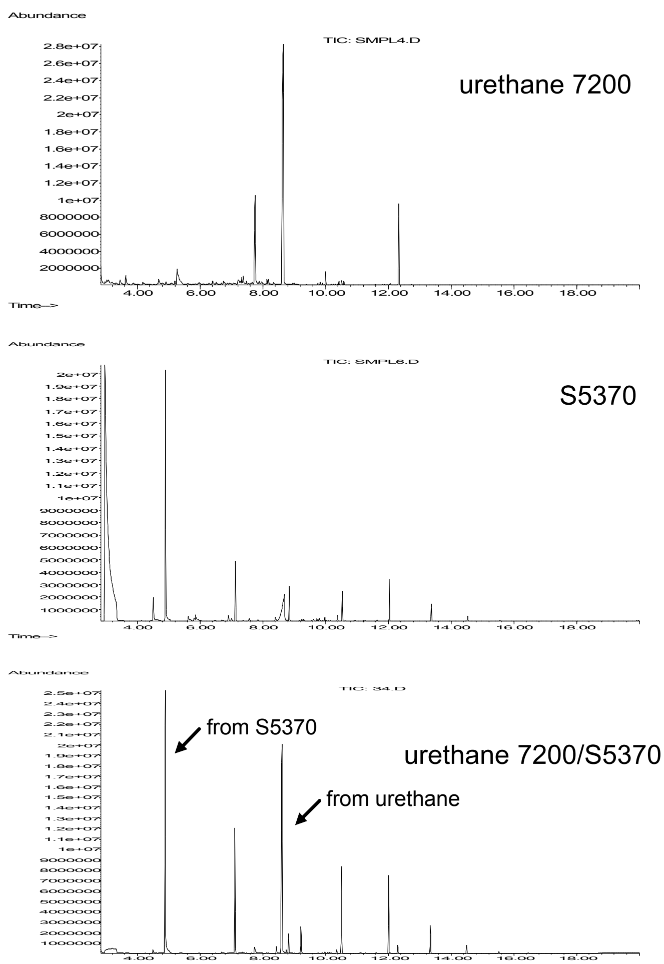

Figure 2. Gas chromatograms of urethane

chromatogram are from the S5370 and urethane 7200, and the other visible peaks are background siloxanes.

Ongoing materials aging and compatibility tests (MAC-1) carried out at Sandia/CA have identified some potential materials of interest, and these will be studied in more detail in FY05. Future microcompatibility tests will focus on materials that display higher levels of outgassing and/or are more sensitive to other species known to be present in the weapon headspace. Finally, new or reformulated materials will be subjected to headspace analysis and compatibility testing.

SPME of polar analytes: Outgassing analysis of the materials listed in Table 3 in the appendix was carried out using a polar polyacrylate SPME fiber and a polar GC column. While most materials did not exhibit significant polar outgassing products, there were some cases where obvious differences were observed in the polar vs nonpolar fibers/columns. Figure 3 shows the different data obtained for a standard polar test mix using columns designed for polar or nonpolar analytes. The polar column leads to strong signals from polar analytes

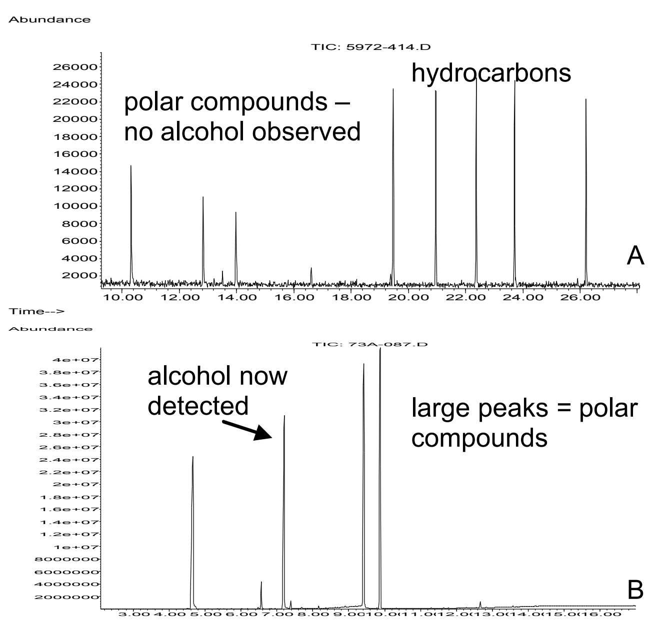

Figure 3. SPME headspace samples of polar test mix
(A = RTX5-MS column; B = Nukol column)

including 1-octanol, which is not observed on the nonpolar column. The most striking example yet observed in initial studies of actual weapon materials is shown in Figure 4 where the presence of benzyl alcohol is detected in removable epoxy foam (REF308). Using the non-polar column, the benzyl alcohol signal virtually disappears in the baseline. Researchers at Sandia believe the benzyl alcohol is probably a minor contaminant in the solvent used during the foam processing, and it is unlikely that benzyl alcohol is present in high enough quantities to be a concern. These early experiments, however, serve to highlight the potential for collecting additional data by focusing on polar analytes.

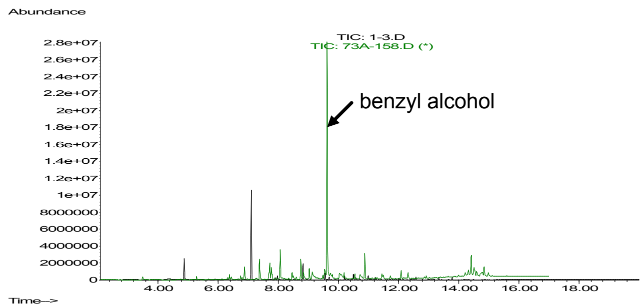

Figure 4. Overlay of chromatograms of

Conclusions

SPME continues to show its usefulness in directed stockpile work. In addition to expanding on work initiated in FY03, we have begun exploring other applications including collection of polar analytes and analysis of large scale compatibility tests such as Sandia's MAC-1 test. SPME GC/MS remains one of the best techniques for the non-destructive analysis of trace outgassing signatures from weapon materials, and it offers the flexibility of tailoring the collection and separation media for specific classes of target analytes. The Weapon Materials Compatibility and Aging group will continue to take advantage of SPME while working to improve and expand its utility in directed stockpile work.

Appendix

Table 1. Individual Materials – SPME Headspace Analysis

Material	Folder
3M 465 adhesive	040621.s
APC 300	040409.s
Butyl Rubber	040617.s
DC745U	040621.s
FM123	040617.s
FPC461	040621.s
Halthane	040409.s
Honeycomb	040409.s
Kapton cable	040617.s
Kel-f 800	040409.s
Loctite A	040621.s
Loctite EV	040621.s
LW520	040617.s
Nylon sleeve	040621.s
Polysulfone	040617.s
Polyurethane	040409.s
S5370	040106.s
Sylgard 184	040409.s
Syntactic polysulfide	041013.s
TPX	040409.s
Urethane 7200	040106.s
Viton A	041013.s

Table 2. Materials subjected to microcompatibility tests (Data for completed tests in folders 040723.s, 040811.s & 040903A.s; Pending tests indicated with X)

	Viton A	S5370	Urethane 7200	Kel-F	OXY461	Sylgard 184	Polysulfone	FPC461	HMX	M97	Silicone foam	silastic	Silastic E	DC745U	Ethylene propylene	mylar	Nitrile buna - N	Polycarbon-ate	DC281	TATB	RDX
Viton A																					
S5370	DONE																				
Urethane 7200	DONE	DONE																			
Kel-F	DONE	DONE	DONE																		
OXY461	DONE	DONE	DONE	DONE																	
Sylgard 184	DONE	DONE	DONE	DONE	DONE																
Polysulfone	DONE	DONE	DONE	DONE	DONE	DONE															
FPC461	DONE	DONE	DONE	DONE	DONE	DONE	DONE														
HMX	X	X	X	X	X	X	X	X													
M97	X	X	X	X	X	X	X	X	X												
Silicone foam	X	X	X	X	X	X	X	X	X	X											
Silastic	X	X	X	X	X	X	X	X	X	X	X										
Silastic E	X	X	X	X	X	X	X	X	X	X	X	X									
DC745U	X	X	X	X	X	X	X	X	X	X	X	X	X								
Ethylene propylene diene	X	X	X	X	X	X	X	X	X	X	X	X	X	X							
Mylar	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X						
Nitrile buna-N	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X					
Polycarbonate	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X				
DC281	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X			
TATB	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X		
RDX	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	

Table 3. Materials sampled with polar SPME fiber and Nukol column.

Material	Data Folder
Polyurethane	0404.s
Sylgard 184	0404.s
Polysulfone	0404.s
TPX	0404.s
Halthane	0404.s
Viton A	0404.s
Kel-F	0404.s
APC	0404.s
Honeycomb	0404.s
REF 308	0406.s
RSF 200	0406.s
Polysulfide	0406.s
Syntactic polysulfide	0406.s
Urethane 7200	0406.s
Loctite A and EV	0406.s